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Structural and Morphological modification of 100 MeV, silver (Ag^{8+}) Swift Heavy Ions Irradiated Polypyrrole

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ABSTRACT

Polypyrrole (PPY) is a conducting polymer that displays rich variety in morphology, partially crystalline, and partially disordered. Investigations are still being pursued to make them more conducting and crystalline. In the present investigation, conducting polymer polypyrrole (PPY) thin films have been prepared by the electrochemical polymerization technique and were irradiated by 100 MeV, silver (Ag^{8+}), swift heavy ions (SHI) at various fluences of 10^{10}, 10^{11} and 10^{12} ions / cm^2. A comparative study of samples before and after irradiation has been performed by using various techniques such as Fourier Transform Infrared Spectroscopy (FTIR), Atomic force microscopy (AFM), X-ray diffraction (XRD). With increase in fluence, the surface structure of PPY films becomes smoother, the crystallinity increases and the conductivity increases by two orders. The present investigations open up the scope for the applicability of irradiated conducting polymers with defined conductivity for sensor applications.

Introduction

Building the new supra-molecular architectures with the desired structures and properties with greater ease of applications has been of great interest in recent years (Roncali J 1992). Polymers have traditionally been considered as a good electrical insulators and a variety of their applications have relied on their insulating property. However in 1977, researchers have shown that certain class of polymers that are conjugated, exhibit semi-conducting behavior (Chiang C K et al 1977). The discovery of doping has led to a further dramatic increase in the conductivity of such conjugated polymers to values as high as 10^5 S/cm. The presence of an extended π conjugation in polymers provides the required mobility to charges that are created on the polymer backbone (by the process of doping) and make them electrically conducting (Singh R K et al 2007). Conducting polymers have become the foci of attention in the field of material science. Among all; polyaniline and polypyrrole have received greater attraction due to their favorable economics, easy synthesis, environmental stability, and unique chemistry (Tallman D E et al 2007). They have been tailored for numerous applications such as electromagnetic interface (EMI) shielding [Kim S H et al 2003; Yang Y et al 2005], environmental sensors [Ma X et al 2008], batteries [Wang Jet al 2005], supercapacitors [An K H et al 2002], fuel cells [Qin H Y et al 2008] and anticorrosion coatings[Yu Y J et al 2002] etc. Applications of these polymers have begun to emerge a new era. The electrical conductivities of the intrinsically conducting-polymer systems range from those insulators ($<10^{-5}$ and 10^{-10} S/cm) to those of typical semiconductors such as silicon ($\approx 10^{-5}$ S/cm) and to those greater than 10^4 S/cm (nearly to that of a good metal such as copper $\approx 5\times10^5$ S/cm).

Polypyrrole should be stable enough to sustain for a longer time in radiations without degradation for its application in sensors. In the present investigation, polypyrrole has been exposed to swift heavy ion beam radiations and changes in its electrical, morphological and structural properties have been analyzed. It was found that the stability of the polypyrrole after irradiations has increased and surface has become smoother. The room temperature conductivity has increased by two orders of magnitude. This is further supported by the XRD measurement which shows the 10% increase in crystallinity after irradiation, which indicates SHI beam irradiated polypyrrole is a good candidate for micro-patterned sensor, in which each micro-patterned sensor can be used for the specific sensing application.

Experimental:

Polypyrrole (PPY) films were deposited on indium-tin oxide (ITO) coated glass by electrochemical polymerization [Singh R et al 1996] of pyrrole monomer. The monomer was doubly distilled before starting the polymerization. The polymerization solution contained 0.1M pyrrole with 0.1M electrolyte tetraethylammonium tetrafluoroborate in propylene carbonate. Before the polymerization, the reaction mixture was thoroughly degassed by passing dry nitrogen for one hour. Polymerization was carried out for 40-60 minutes with current density of 1mA/cm^2 at 273K in an inert atmosphere with slow bubbling of nitrogen gas. The fully doped films of thickness ≈ 15 µm were peeled off and thoroughly washed in deionized water. For dedoping of the polymer, the films were kept in liquid ammonia for 24 hr. The films were sectioned into small samples of 1cm^2 and pristine is marked as (a) while others have been exposed to SHI beam of 100 MeV silver (Ag^{8+}) at three different fluences of 10^{10}(b), 10^{11}(c), 10^{12}(d) ions/cm^2 at Inter University Accelerator centre (IUAC) New Delhi, India.

The samples has been characterized by different techniques such as X-ray diffraction that has been recorded by a Bruker AXS x-ray diffractometer with Cu-Kα radiation (1.54 Å) for a wide range of Bragg's angle 2θ ($5^o < 2\theta < 40^o$). Atomic Force Microscopic (AFM) images have been taken on Nanoscope IIIa in tapping mode. FTIR data was recorded on Perkin Elmer FTIR Spectrophotometer.

Results and Discussion:

100 MeV energy of silver (Ag^{8+}), swift heavy ions (SHI) radiations has been chosen for the present investigations. The Stopping Range of Ions in Matter (SRIM 2006) for 100 MeV Ag ions in the sample was estimated by program by J. P. Biersack and J. F. Ziegler [Ziegler J F et al 2008]. In swift heavy ion beam irradiation the loss of the energy of the incident ions in target material is through electronic energy loss and nuclear energy loss. Fig. 1 (a) shows the variation of electronic energy loss ($S_e = dE/dx_e$), and nuclear energy loss ($S_n = dE/dx_n$) with the variation of energy of incident ions. The calculated range (Fig.1(b)) for 100 MeV Ag ions is ≈ 20.89µm, the electronic energy loss ($(dE/dx)_E$) and nuclear energy loss ($(dE/dx)_N$) are $8.6x10^3$ & 35.4 eV/ nm respectively.

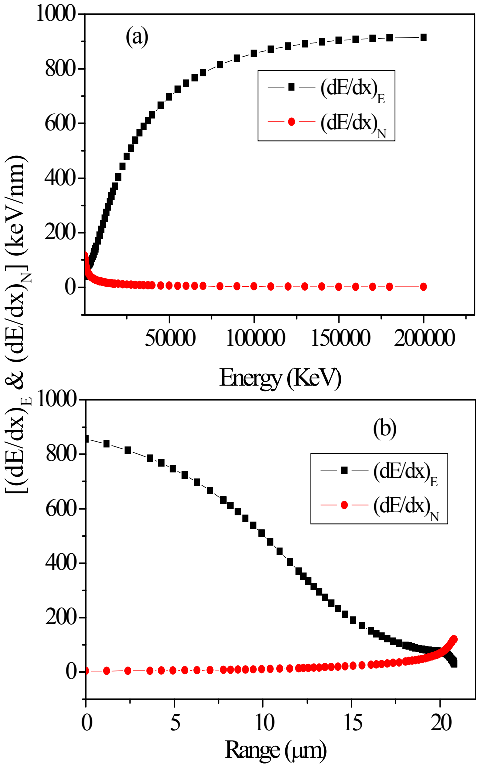


Fig.1: Variation of Electronic and Nuclear Energy loss with (a) Energy and (b) Range.

So, electronic energy loss dominates over nuclear energy loss. Since, the range is larger than the film thickness (15 µm), the ions will pass through the substrate. However the ions during their transit modify the film. The energy of the ions used is so high that the energy loss of the ions in the film is dominantly due to inelastic collisions with the electrons leading to electronic excitation or ionization, whereas the energy loss in the elastic collisions is significantly smaller as seen by Monte-Carlo simulation program SRIM.

Fourier Transform Infrared Spectroscopy:

The FTIR spectra of pristine and swift heavy ion beam irradiated polypyrrole samples is shown in Fig. 2 are almost same, i.e. no significant change has been observed in characteristic peak position of the polymer irradiated at the different fluences, upto 10^{12} ions/cm^2.

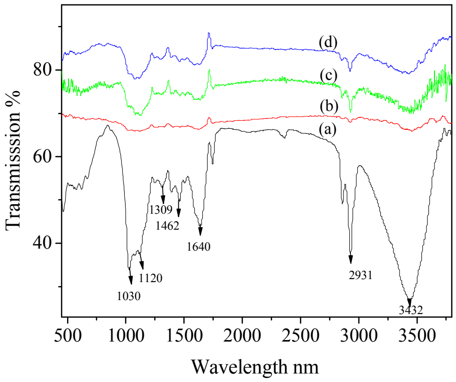


Fig.2 FTIR spectra of pristine (a) and 100MeV Ag^{8+} ions irradiated polypyrrole polymer at the various fluences of 10^{10} ions/cm^2(b), 10^{11} ions/cm^2 (c) and 10^{12} ions/cm^2 (d).

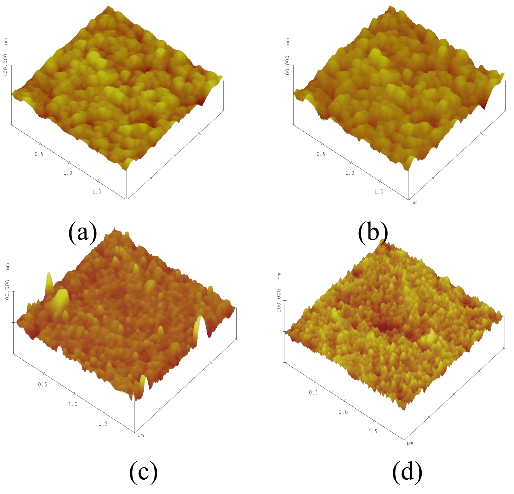
This signifies that the polymer retains its chemical structure after irradiation. The main vibrational modes for electrochemically-synthesized SHI irradiated polypyrrole polymer has been given in Table 1 [Singh R et al 1996]. However, the intensity and disappearance or broadening of some bands can be attributed to the chain scissoring and cross-linking in the polymer due to irradiation of energetic SHI beam.

Table: 1. Band assignment of (a) and irradiated polypyrrole polymer at the various fluences of 10^{10} ions/cm^2 (b), 10^{11} ions/cm^2 (c) and 10^{12} ions/cm^2 (d).

Band Assignment	Reference (12)	Pristine	10^{10} ions/cm^2	10^{11} ions/cm^2	10^{12} ions/cm^2
N-H	3408	3432	3432	3432	3432
C-H	3110	2931	2931	2931	2931
C=C	1547	1640	1640	1640	1640
C-C	1441	1462	1462	1462	1462
C-N	1309	1309	1309	1309	1309
C-H (def.)	1043	1030	1030	1030	1030

Atomic Force Microscopy:

AFM picture of pristine polypyrrole has been given in Fig. 3(a). As expected, cauliflower morphology has been observed. This fractal type growth has been obtained earlier also [Singh R et al 1996] and has been attributed to 3D type growth. When the current flows uniformly to the electrode, the polymer grows concentrically. However a small non-uniformity, even of few nanometers, may give rise to tiny nodules or hump on the surface of growing polymer. The electric field increases in that region, thereby increasing the current, which further enhances the growth of the nodule that further increases the electric field. This continues till a critical size is reached and then the field strength on surface of nodule decreases. The condition is same as the beginning, so the next nodule starts growing. The AFM picture of irradiated samples are given in Fig. 3 (b), (c), and (d), respectively. It is evident from these images that irradiation causes the restructuring of the polymer. The surface becomes smoother with increase of ion fluence. The cauliflower morphology also disappears with increasing fluence [Kaur A et al 2009].



(a) (b)

(c) (d)

Fig.3: AFM images of pristine (a) and 100MeV Ag^{8+} ions irradiated polypyrrole polymer at the various fluences of 10^{10} ions/cm^2 (b), 10^{11} ions/cm^2 (c) and 10^{12} ions/cm^2 (d).

Conductivity and X-ray diffraction:

The conductivity of pristine sample has increased by two orders of magnitude after irradiation as given in Table 2. The increase in conductivity can be attributed to ordering of the polymer chains due to displacement of atoms, and the chains may become more compact due to irradiation.

Table: 2. Conductivity at room temperature and percentage of crystallinity in pristine (a) and irradiated (b), (c), (d) Polypyrrole.

Sample name	**Fluence ions/cm^2**	**σ_{dc} S/cm at (300K)**	**% of Crystallinity in PPY**
(a)	Pristine	6.52X10^{-7}	30.85
(b)	10^{10}	4.58X10^{-6}	36.75
(c)	10^{11}	1.66X10^{-5}	40.74
(d)	10^{12}	9.43X10^{-5}	41.94

This is further supported by X-ray diffractograms of unirradiated and irradiated samples, (Fig. 4), the intensity of peaks increases with fluence. By calculating the ratio of the area under peaks to the total area of the peaks it has been observed that degree of crystallinity increases with fluence and this change is about 10% for 10^{12} ions/cm^2. The increased degree of crystallinity leads to higher values of conductivity due to decreased scattering of charge carriers. However, the peaks are not as sharp as that for conventional crystalline materials, the polymer is predominantly amorphous in nature and the chains have been more organized due to irradiation.

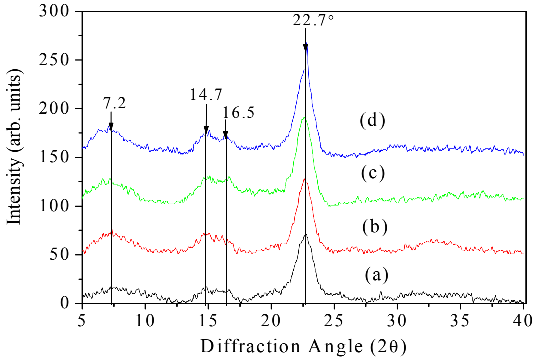


Fig.4: XRD spectra of pristine (a) and 100MeV Ag^{8+} ions irradiated polypyrrole polymer at the various fluences of 10^{10} ions/cm^2(b), 10^{11} ions/cm^2 (c) and 10^{12} ions/cm^2 (d).

Conclusions:

The influence of SHI, on polypyrrole polymer has modified the texture of the films. The samples become smooth textured. The conductivity has increased by about two orders of magnitude that are attributed to better organization and reordering of chains as observed by XRD. While by FTIR spectroscopy confirms that original structure of the polymer is retained even after irradiation. Most importantly the polymer is found to be stable for about a year which supports the applicability of the material after irradiation for device fabrication such as batteries, fuel cells, supercapacitors, sensors and EMI shielding.

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